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Kinetic study of dehydration in gel grown iron tartrate dihydrate crystals

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Abstract : The sperulitic crystals of iron (II) tartrate dihydrate were grown by the gel method. The kinetic analysis of the thermogravimetric data was carried out by using Coats-Redfern, Horowitz-Metzger and Freeman-Carroll relations. The values of activation energy, order of reaction, frequency factor and entropy were calculated for the dehydration process in the crystals.

Keywords : Spherulitic crystals, thermogravimetric analysis, kinetic parameters.

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1. Introduction

Thermogravimetric Analysis (TGA) is widely used for rapidly assessing the thermal stability of different substances. Thermogravimetric analysis has been carried out on variety of substances, for example, calcium oxalate monohydrate [1–3], thorium and uranium (VI) 8-quinolinol chelates [4], and double ammonium hexahydrate salts of some metals [5]. Apart from this, many other workers have applied the TGA to study the thermal properties of different crystals, such as hydrated cadmium oxalate crystals [6], calcium tartrate single crystals [7], neodymium tartrate single crystals [8] and bismuth oxalate crystals [9].

In the present communication, the kinetic parameters are deduced from the TGA curve for the gel grown spherulitic crystals of iron (II) tartrate dihydrate.

2. Experimental techniques

A test-tube diffusion method was employed to grow iron (II) tartrate dihydrate crystals in a gel medium. One of the reactants 1M tartaric acid was mixed with sodium metasilicate to prepare the gel. After setting the gel, the supernatant solutions of hydrated ferrous sulphate in the range of 0.5 M to 1.5M were slowly poured without disturbing the gel surfaces.

Spherulitic crystals of iron (II) tartrate dihydrate were grown within a period of one month. The good quality crystals were grown in the pH range of 3.8 to 4.2 and with the specific gravity range of 1.06 to 1.075 at room temperatures. However, the best quality crystals were grown at a pH of 4, specific gravity of 1.075 and with ferrous sulphate solution of 1M concentrations. Details of the crystals grown, have been reported elsewhere [10]. Figure 1 shows the types of spherulitic crystals grown.

The thermogravimetric analysis was carried out by using TGS-2 Perkin Elmer thermal analyser. The analysis was performed from the room temperature to 850°C at a heating rate of 15°C/min in the atmosphere of air, using α-Al_2O_3 as a reference material. Powdered samples were used in this study.

3. Results and discussions

The use of thermogravimetric data to evaluate kinetic parameters of solid-state reactions involving weight loss, has been investigated by many workers [1–3, 11]. Many times, the pyrolysis occurs through a many stepped mechanism. The shape of the curve is determined by the kinetic parameters of the pyrolysis, such as reaction order, frequency factor and energy of activation. Kotru *et al* [8] reported the kinetics of solid state decomposition of neodymium tartrate. They also calculated values of various kinetic parameters and suggested that the decomposition progressed according to cylindrical kinetic model.

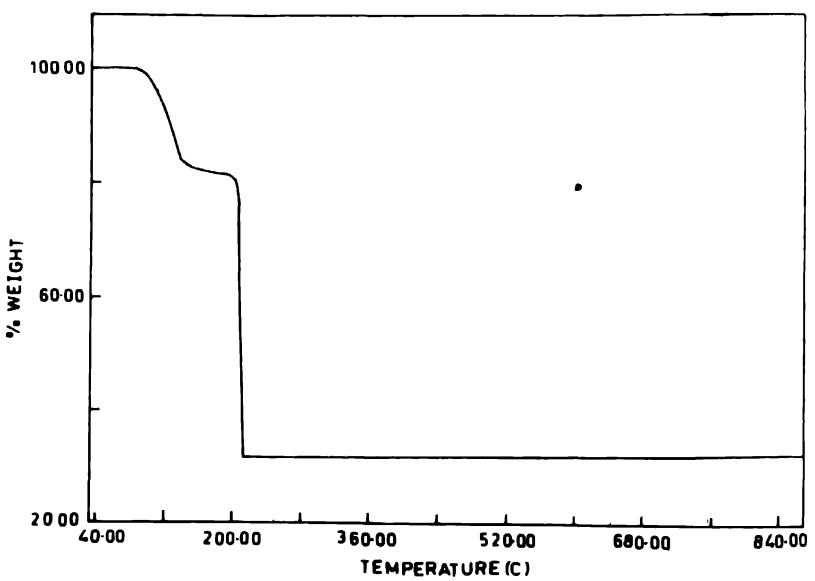

Figure 2. Thermogravimetric curve of iron (II) tartrate dihydrate.

Good quality crystals were picked up from the bottom of the gel in the test tubes. The thermogravimetric curve for this crystals is shown in Figure 2, which suggests that the decomposition is quite simple in the case of iron (II) tartrate. Starting with hydrated

Plate I

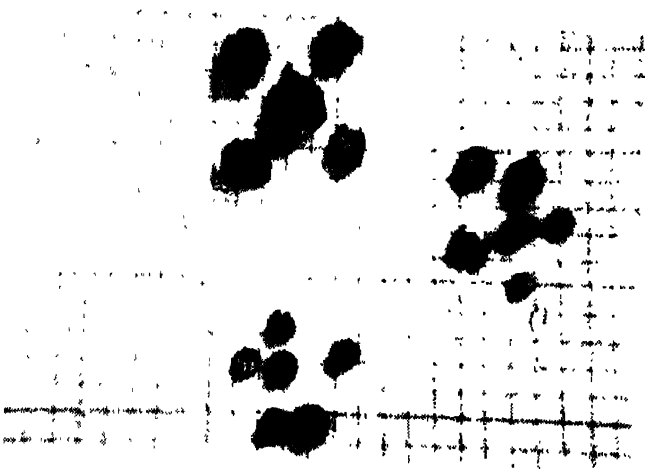

Figure 1. The types of spherulitic crystals of iron (II) tartrate dihydrate grown by the gel method

samples, the first stage is dehydration and the final stage is decomposition to ferrous oxide. Two water molecules were found to be present in the initial hydrated sample [10].

In the present investigation, three different equations are applied to evaluate the kinetic parameters from the TG curve of Figure [2]. These equations are applied to the first stage of the decomposition *i.e.* dehydration, since the second stage shows very rapid weight loss with the temperature and also it is difficult to assume the initial weight for the second stage of decomposition process.

Coats and Redfern [3] derived the following equation to determine the values of activation energy and order of the reaction.

$$\log_{10}\left[\left\{1-(1-\alpha)^{1-n}/T^2(1-n)\right\}\right] = \left\{\log_{10}\left[AR/aE\right]\left[1-2RT/E\right]\right\} - \left\{E/2.3RT\right\}, \quad (1)$$

where α = fraction of the original substance decomposed at time t,

n = order of the reaction,

A = frequency factor,

E = activation energy of the reaction,

R = gas constant and

a = heating rate in deg. min^{-1}.

To determine the value of activation energy and order of the reaction, the plot of $\log_{10}$ $[\{1-(1-\alpha)^{1-n}\}/\{T^2\ (1-n)\}]$ versus $1/T$ is drawn for different values of n and the best linear plot gives the correct values of n. This equation is valid for all values except $n = 1$. Figure 3 is the plot for this equation. The values of activation energy, frequency factor and the order of the reaction were found to be 82.06 $KJmol^{-1}$, 1.13×10^{22} and 3/2 respectively.

Horowitz and Metzger [2] obtained an equation for the pyrolysis where only a fraction of the total weight is lost as in the loss of water of hydration from a hydrated salt. If W is the weight remaining at a given temperature and W_o and W_f are the initial and final weights, respectively, then

$$C = (W - W_f)/(W_o - W_f). \quad (2)$$

Further, using this equation, the following equation was derived by Horowitz and Metzger [2].

$$\log_{10}[1-C^{1-n}/1-n] = E\theta/2.303RT_s^2, \quad (3)$$

where, E = activation energy,

n = order of the reaction and

R = gas constant.

Here T_s is chosen from the curve of C versus T, where the value of dC/dt is maximum. Also, the following equation suggests the relationship between θ and T_s,

$$T - T_s = \theta. \quad (4)$$

A plot of the left hand side of eq. (3) versus θ gives best fit straight line with its slope equal to E/RT_i^2. Figure 4 shows this plot. From the plot, the values of activation energy and order of reaction were calculated to be 103.64 KJMol^{-1} and 3/2, respectively.

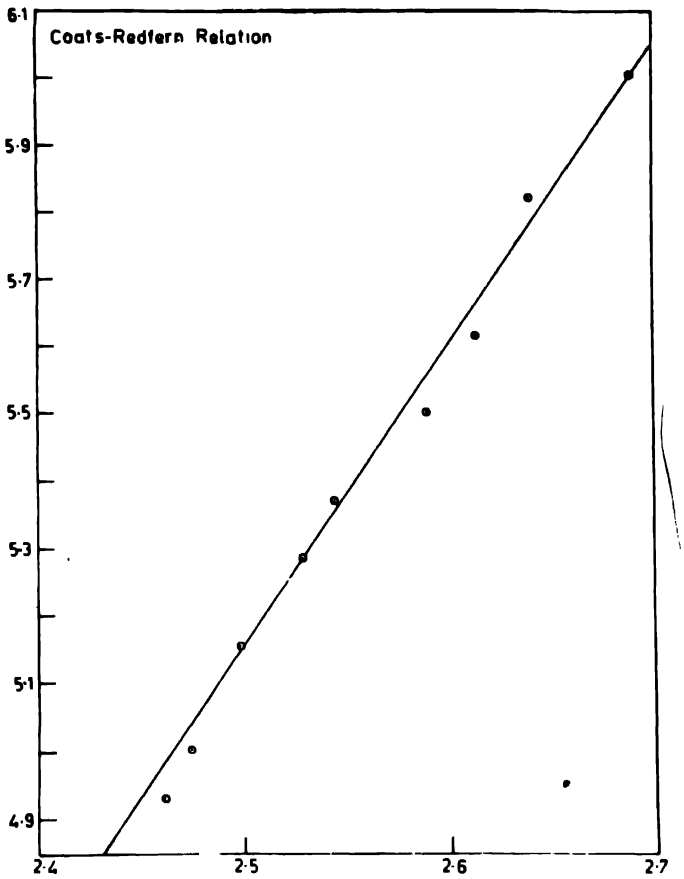

Figure 3. A plot for Coats-Redfern relation, where $Y = -\log [\{1-(1-\alpha)^{1-n}\}/T^2 \times (1-n)]$ and $X = 1/T \times 10^3$ in K^{-1}.

Another important equation to calculate the kinetic parameters was derived by Freeman and Carroll [1]. They used this equation to calculate the values of order of the reaction and energy of activation for dehydration and decomposition of $CaC_2O_4 . H_2O$ and $CaCO_3$. The equation is as follows :

$$\left[\{-E/2.3R\Delta(1/T)\} / \{\Delta \log W_r\}\right] = -x + \left[\{\Delta \log dW/dt\}\right] / \{\Delta \log W_r\}\}, \quad (5)$$

where W_c = Weight loss at the completion of the reaction,

W = total weight loss up to time t,

T = absolute temperature,

R = gas constant,

E = activation energy and

x = order of the reaction.

Here, W_r is estimated from the following equation

$$W_r = W_c - W. \tag{6}$$

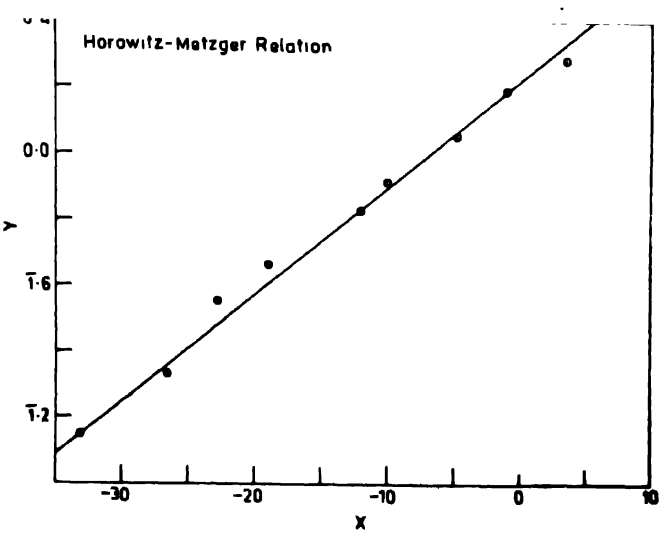

Figure 4. A plot for Horowitz-Metzger relation, where $Y = \log [(1 - C^{1-n})/(1 - n)]$ and $X = \theta$.

Figure 5 is a plot of $[\Delta \log (dW/dt)]/\Delta \log W_r$ versus $\Delta (T^{-1})/\Delta \log W_r$ for the dehydration process of iron (II) tartrate dihydrate, which is a straight line and the values of the order of the reaction and activation energy are found to be 3/2 and 27.34 $KJMol^{-1}$ respectively.

The value of entropy can be computed using the equation [8]

$$A = \left(kT_m/h\right)e^{S/R}, \tag{7}$$

where k = Boltzmann constant,

h = Plancks constant,

A = frequency factor and

S = entropy.

Using the value of frequency factor obtained from eq. (1), the entropy is found to be 174.72 $JK^{-1}Mol^{-1}$ Except for eq. (1), other equations do not give values of the frequency factor.

Table 1 summerizes the results obtained from all the three equations. It can be observed that the order of reaction remains the same, whereas the value of activation energy varies for all the three analysis. The value of activation energy is comparatively low in the

case of Freeman-Carroll relation. The variation in the values of activation energy may be due to different mathematical treatments applied to explain the decomposition mechanism.

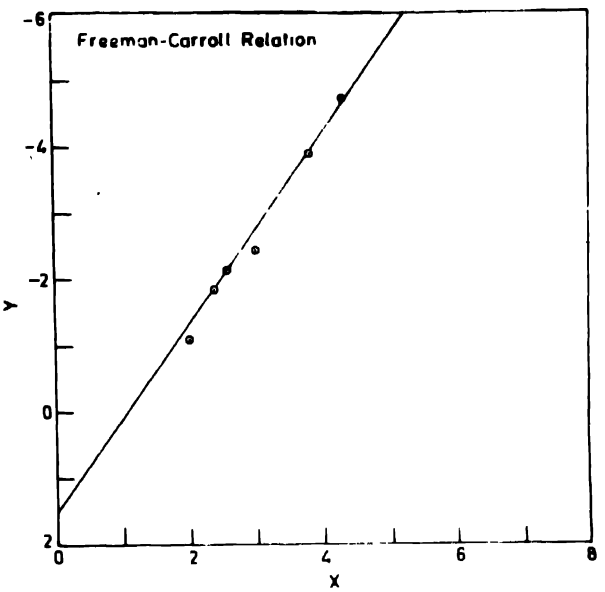

Figure 5. A plot for Freeman-Carroll relation, where $Y = (\Delta \log dW/dt)/(\Delta \log W_r)$ and $X = (\Delta T^{-1})/(\Delta \log W_r)$

Freeman and Carroll [1] analysis uses the techniques of differential thermal analysis for evaluating the kinetic parameters in order to eliminate the trial and error procedure, while Horowitz and Metzger [2] incorporates an approximate integral method similar to Van Krevelan *et al* [11] from which pyrolysis parameters can be easily extracted. Moreover,

Table 1. The values of order of reaction and activation energy for different kinetic relations.

Relation used	Order of the reaction (n)	Activation energy $KJMol^{-1}$
Coats-Redfern relation	3/2	82.06
Horowitz-Metzger relation	3/2	103.64
Freeman-Carroll relation	3/2	27 34

comparatively less difference in the values of activation energy in both Horowitz-Metzger as well as Coats-Redfern relations, further suggests that the decomposition proceeds according to the contracting cylinder model [8,12].

4. Conclusions

Three kinetic relations, *viz.* Coats-Redfern, Horowitz-Metzger and Freeman-Carroll were applied to the dehydration of gel-grown iron (II) tartrate dihydrate crystals and kinetic parameters, such as the order of reaction, the frequency factor and the activation energy were calculated. The order of reaction was found to be constant 3/2 in all the relations, while the activation energy varied from 27.34 $KJMol^{-1}$ to 103.64 $KJMol^{-1}$. This is understood due to different mathematical treatment applied to explain the decomposition process in different models. Also, the close relationship between Horowitz-Metzger and Coats-Redfern relations suggests that the decomposition proceeds to the contracting cylinder model.

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